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14. ABSTRACT Many high-temperature composite resins, such as cyanate esters, require high temperatures in order to achieve complete cure. In such situations, incomplete conversion often persists in completely solidified "cured" samples, leading to potentially significant degradation in performance. Moreover, the very steep dependence of the glass transition temperature of the composite resin on the extent of cure leads to unusual cure effects such as 1) significant cure below the glass transition temperature 2) cure kinetics that involve extremely strong temperature dependence coupled with very weak dependence on cure time, and 3) unexpected conversion-property relationships (e.g. a decrease in elastic modulus with increasing extent of cure). These effects not only complicate the prediction of composite performance, they also make the determination of even simple properties such as the extent of conversion or glass transition temperature prone to large, difficult-to-detect errors. This paper describes and demonstrates newly developed characterization methods that combine multiple techniques to overcome these difficulties, and allow for a more complete description of the evolving glass transition temperature of composite resins during part fabrication, testing, and performance. In addition, the paper describes how insights into the unusual phenomena associated with resins that cure at high temperature can lead to design strategies for high-temperature composite resins that provide optimal performance.					
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POST-VITRIFICATION CURE KINETICS OF HIGH TEMPERATURE COMPOSITE RESINS: IMPLICATIONS FOR CHARACTERIZATION AND PERFORMANCE

9 May 2013

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Outline



- Background: Cure Below T_G and Its Effect on Structure-Property Relationships in Thermosetting Polymer Networks
- Tools: Differential Scanning Calorimetry
- Results:
 - Isothermal Cure Kinetics
 - Validity of T_G Estimation by DSC
 - Results for Dicyanates (BADCy) and Tricyanates (ESR-255)
 - Non-Isothermal Cure Kinetics
 - Dimensionless Analysis
- Implications for Composite Process Development



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Cyanate Esters for Next-Generation Aerospace Systems



Glass Transition Temperature
200 – 400 °C (dry)
150 – 300 °C (wet)

Resin Viscosity
Suitable for
Filament
Winding / RTM

Compatible with
Thermoplastic
Tougheners and
Nanoscale
Reinforcements

High T_g

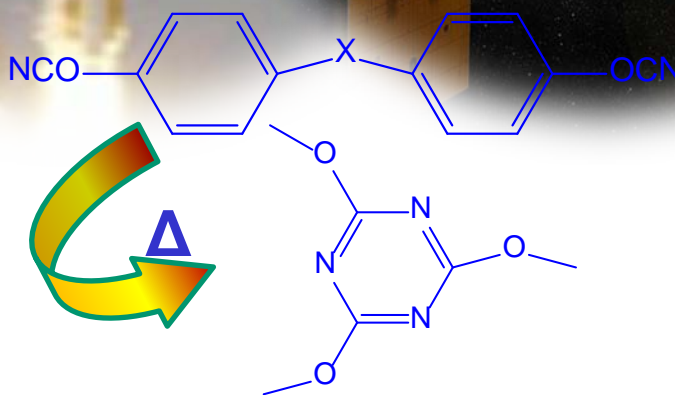
Onset of Weight
Loss:
> 400 °C with High
Char Yield

Good Flame,
Smoke, &
Toxicity
Characteristics

Low Water Uptake
with Near Zero
Coefficient of
Hygroscopic
Expansion

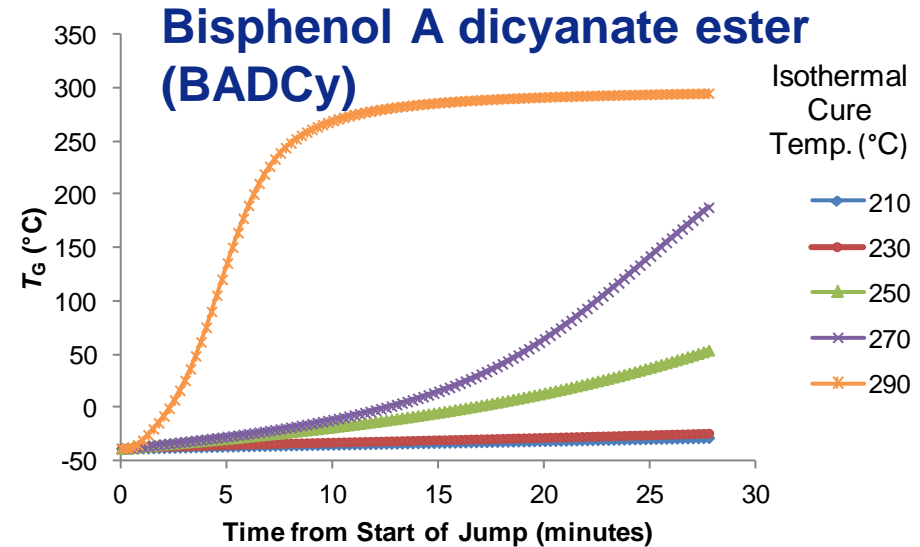
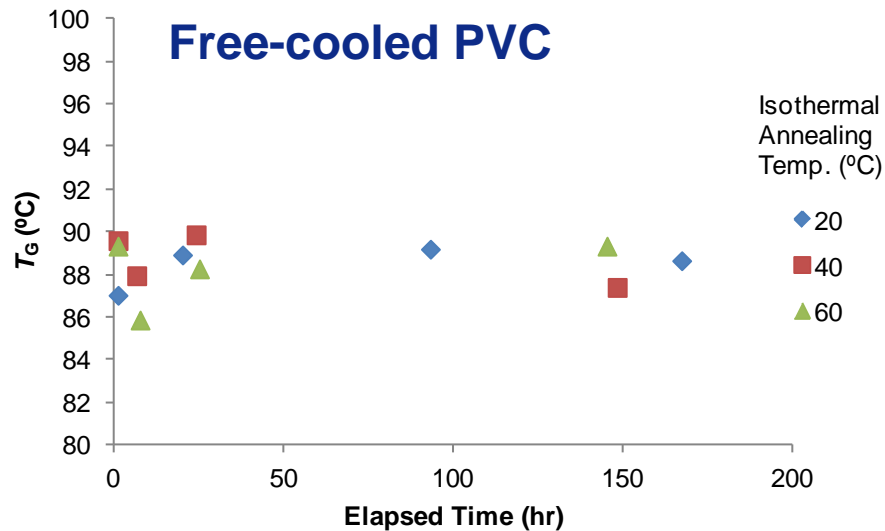
Ease of
Processing

Resistance to
Harsh
Environments





Thermosetting Polymers Have a T_g Envelope – Not Just a T_g

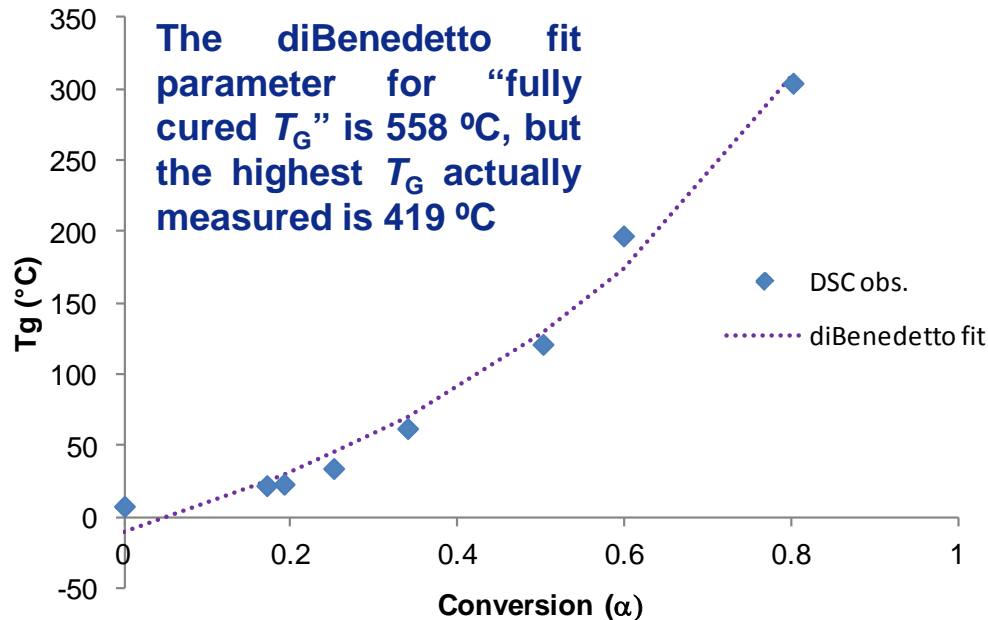


A. R. Berens and I. M. Hodges, *Macromolecules* 1982, 15, 756 (digitized data from Fig. 2)

- The glass transition temperature of a thermoplastic such as PVC exhibits a nearly fixed value regardless of processing-induced changes to the system
- In contrast, the glass transition temperature of a thermosetting polymer can vary over a wide range of temperatures depending on how the polymer is processed
- For cyanate esters, the bounds of the T_g envelope are typically well-defined because of the well-defined cure chemistry



The Envelope May Be Unknown – Some Monomers Can Not Cure Fully

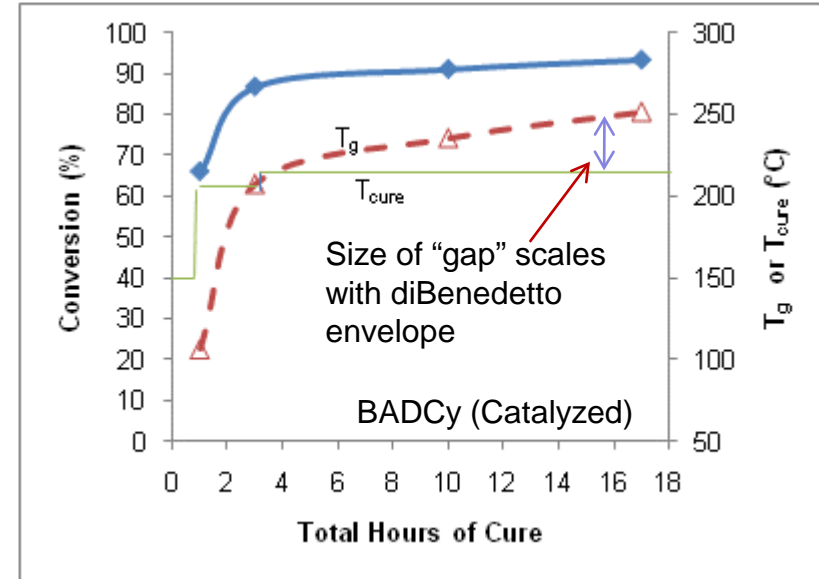
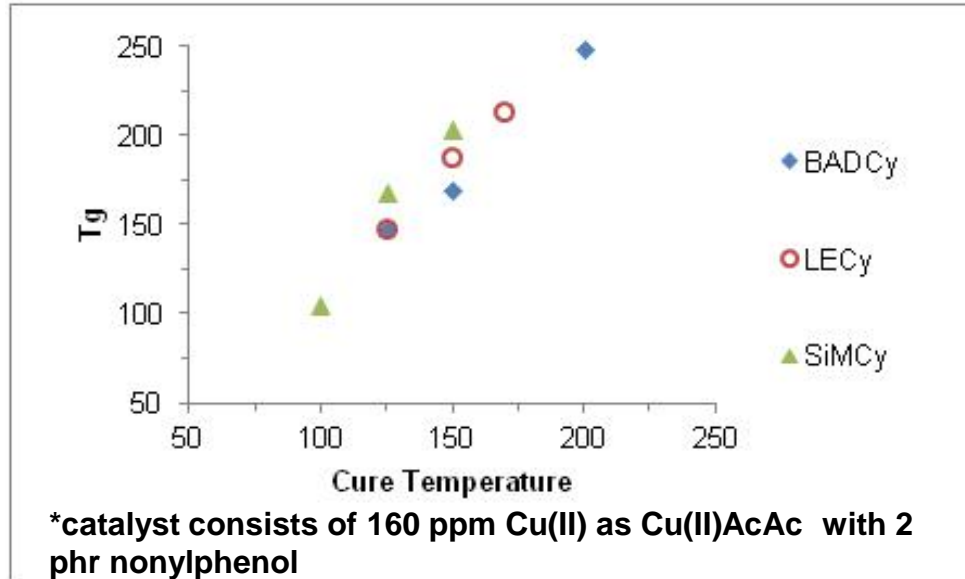


Conversion determined via combined DSC/IR

- Essentially, ESR255 forms such a rigid macromolecular network that the molecular strain energy needed to connect all the loose ends is great enough to break the chemical bonds, so “full cure” simply is not geometrically possible
- Since achieving complete cure is critical for the long-term hydrolytic stability of cyanate esters, a monomer such as ESR255 is actually too rigid by itself
- Even if they can be fully cured, rigid cyanate esters often require very high temperatures and/or active catalysts (which hurt stability) to cure effectively



A Large diBenedetto Envelope Means T_G Exceeds T_{cure} at Late Stages of Cure



T_G (°C) of Cyanate Esters Cured 12 h

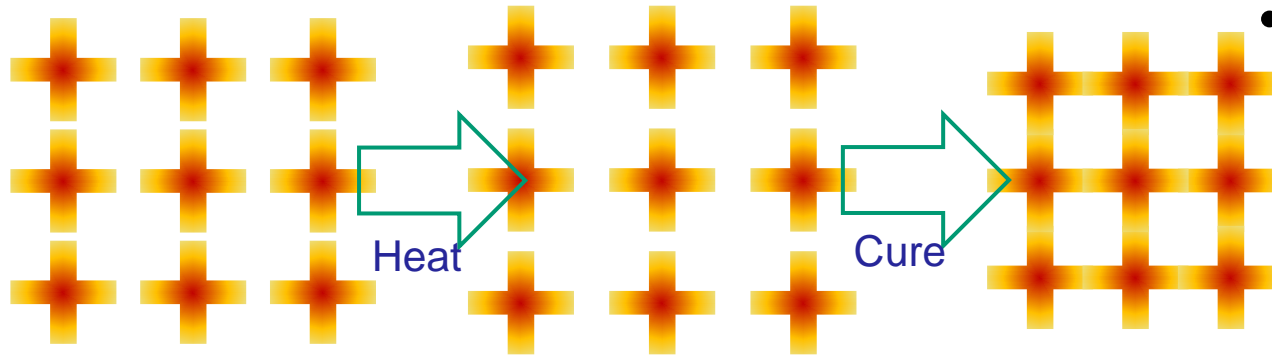
T_{Cure} (°C)	125	150	170	200
BADCy	134	168	--	246
LECy	142	183	213	--
SiMCy	152	186	--	--

- Vitrification slows down conversion, but does not stop it completely
- Under isothermal conditions, the rate of conversion will fall as conversion increases, but the sensitivity of T_G to conversion will rise, resulting in a fairly constant rise in T_G
- The greater the sensitivity, the further T_G can rise above T_{cure}



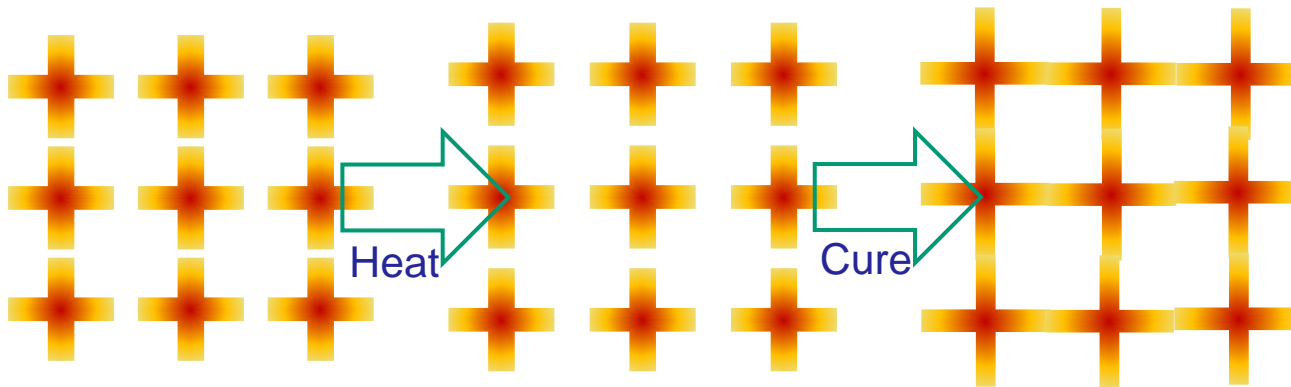
“Vitreous Cure” Differs Markedly from Main Stage Cure

Main Stage Thermal Cure



- Cure results in:
 - *Net Shrinkage*
 - *Less permeability*
 - *Higher modulus*
 - *Brittleness*

“Vitreous Cure”

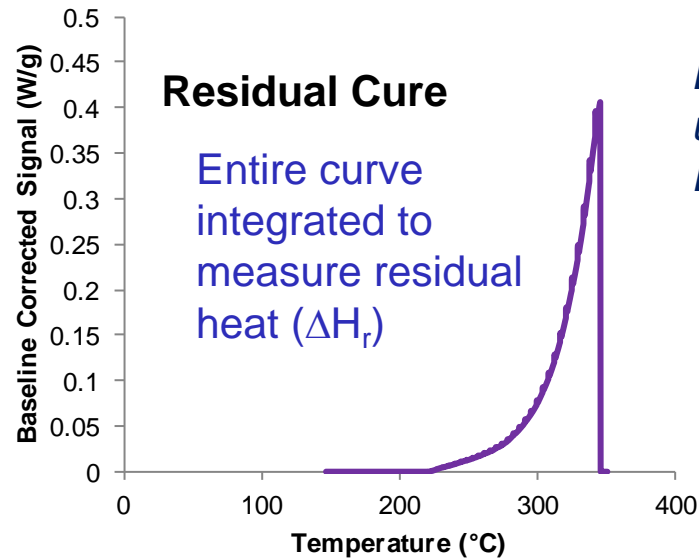
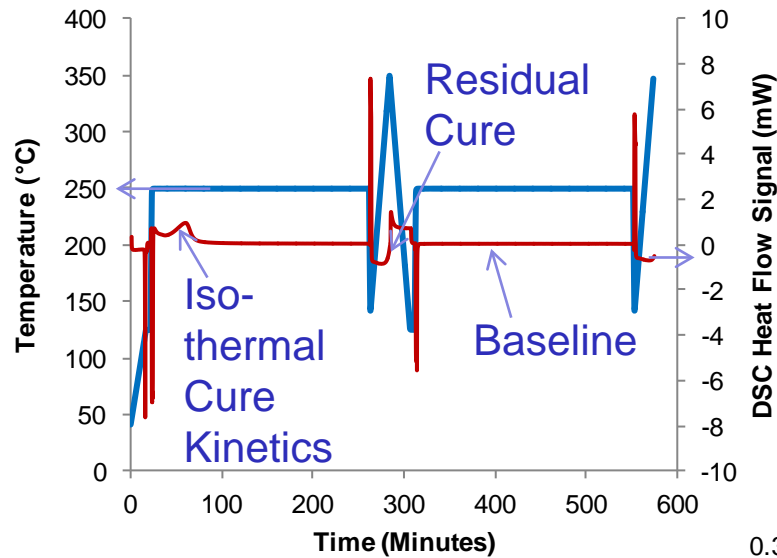


- Cure results in:
 - *Net Expansion*
 - *Higher permeability*
 - *Lower modulus*
 - *Toughness*

- “Vitreous Cure” is promoted by rigid network segments with well-distributed extensibility, and by cure temperatures that are low in comparison to T_G
- Both types of cure can happen sequentially, simultaneously, or in mixed form

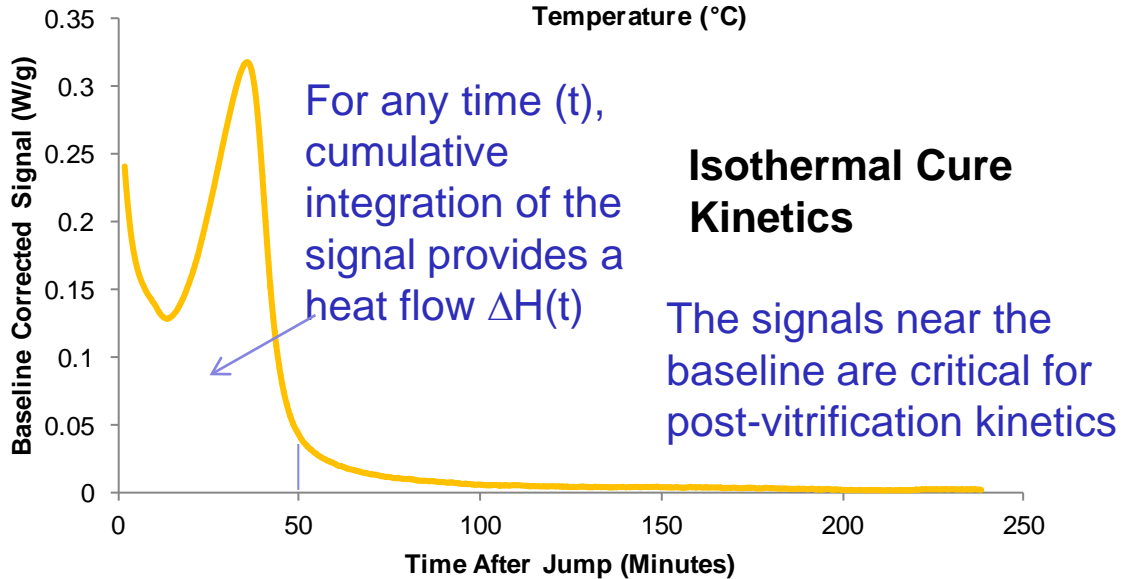


Indirect Measurement of T_G via DSC and diBenedetto Equation



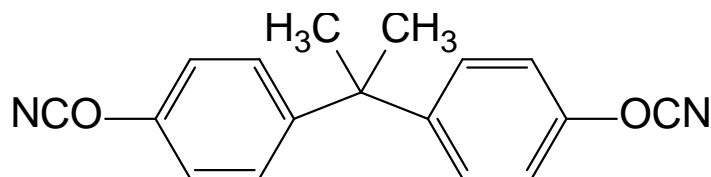
- Conversion computed via:
 $\alpha(t) = \Delta H(t) / [\Delta H(t_{\max}) + \Delta H_r]$
- T_G computed via:

$$\frac{T_G(t) - T_{G0}}{T_{G\infty} - T_{G0}} = \frac{\lambda \alpha}{1 - (1 - \lambda) \alpha}$$

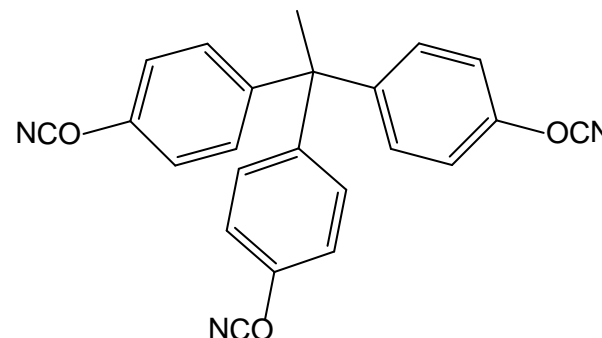




Cyanate Ester Monomers Used in DSC Cure Study



“BADCy”



“ESR-255”

Name	$T_{G0}(^{\circ}\text{C})^*$	$T_{G\infty}(^{\circ}\text{C})^*$	λ	Catalyst Added?
BADCy	-38 ± 1	300 ± 3	0.38 ± 0.04	Yes
ESR-255	-9 ± 10	558 ± 40	0.32 ± 0.04	No

*catalyst consists of 160 ppm Cu(II) as Cu(II)AcAc with 2 phr nonylphenol

- BADCy was the first-commercialized cyanate ester; it is least expensive and has the largest property database
- ESR-255 was originally synthesized and characterized by Shimp; it has the one of the highest “ $T_{G\infty}$ ” values known (note that chemical degradation takes place well below $T_{G\infty}$, thus the parameter is meaningful only as an estimate of the sensitivity of T_G to conversion).

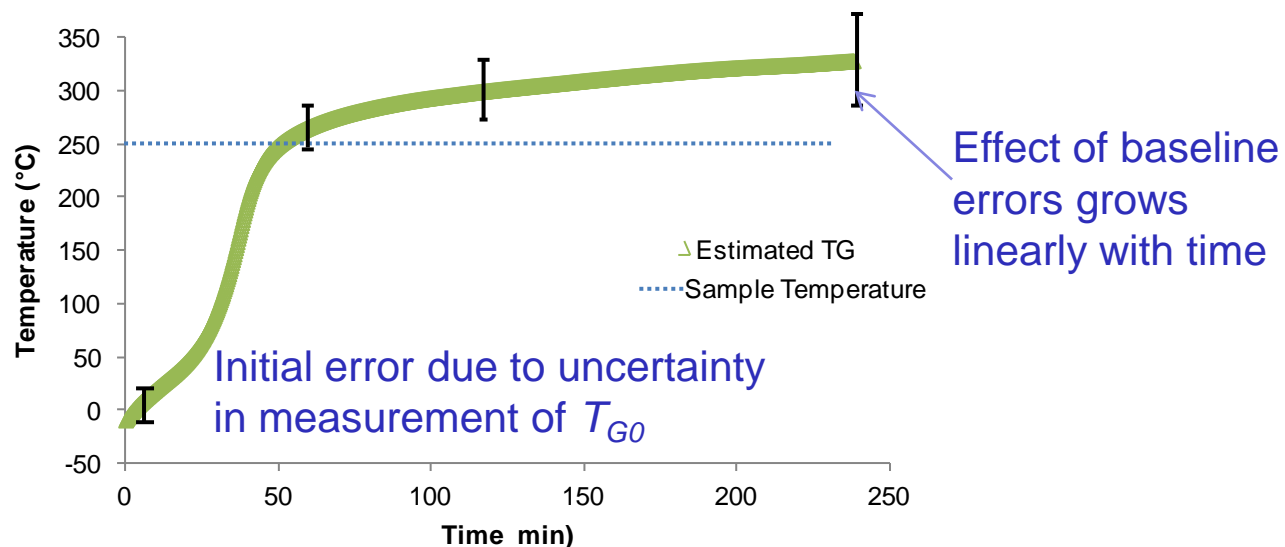


Indirect Measurement of T_G via DSC: Measurement Uncertainties



If DSC measurements were used to generate diBenedetto parameters, then there is a canonical relation for the error in T_G measurement due to all parameters combined.

Data is for uncatalyzed ESR-255



- Even though the error in T_G estimation is large in this case, it is clear that ESR-255 will cure to a T_G substantially higher than the cure temperature, and that the change in T_G with time is substantial even during the post-vitrification period
- Baseline effects become more important than diBenedetto parameter uncertainties after 1-2 hours of isothermal cure
- Sensitivity analysis is the easiest way to determine effect of baseline uncertainties



Comparison of Indirect and Direct T_G Measurements via DSC



Data for catalyzed BADCy

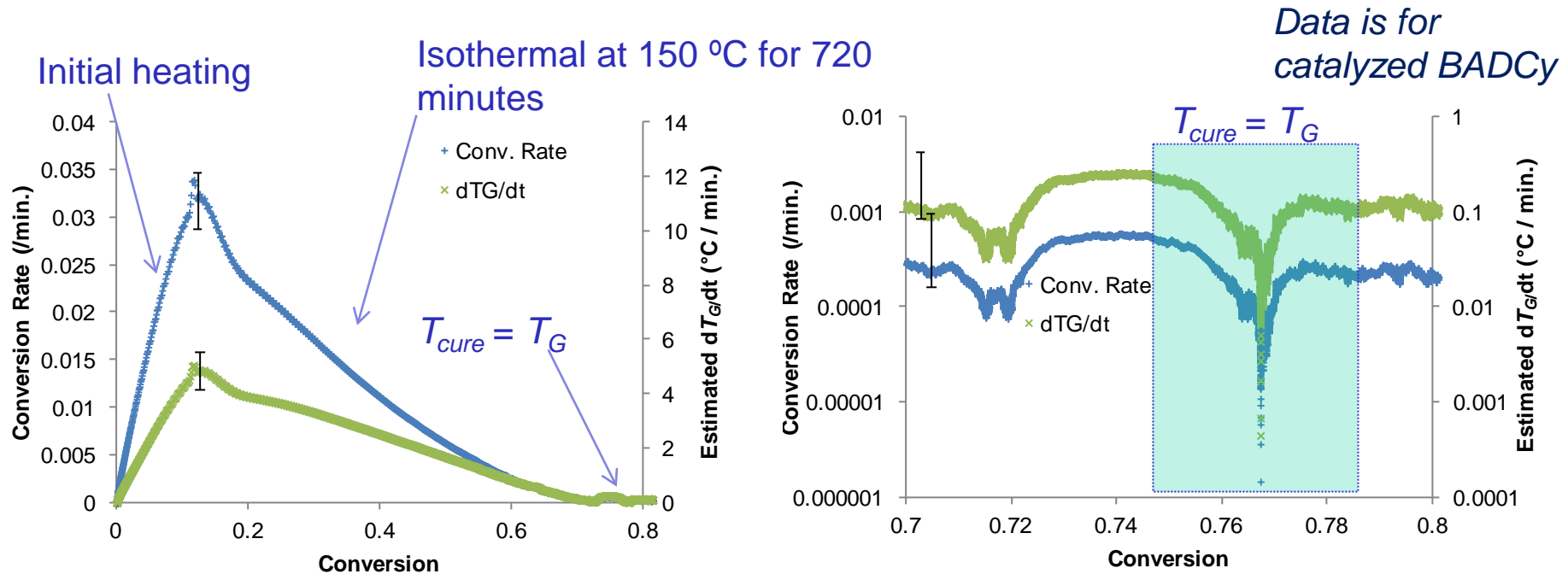
Source (Pred. from iso. DSC run, or “observed”)	T_G after curing for temp. (°C) / time (min.)				
	150/60	150/120	150/720	200/30*	200/720*
Pred. 150 °C / 60 min.	107 ± 9	--	--	--	--
Pred. 150 °C / 1200 min.	114 ± 9	143 ± 9	--	--	--
Pred. 150 °C / 720 min.	90 ± 22	114 ± 24	170 ± 14	--	--
Pred. 200°C / 30 min.*	113 ± 9	--	--	174 ± 9	--
Pred. 200°C / 720 min.*	120 ± 22	--	--	192 ± 36	229 ± 8
Observed T_G	110	144	168	206	246

* Two step cure in which step 1 is 150 °C for 60 minutes

- “Hind-casting” T_G values becomes uncertain when the ratio of elapsed time at the point of “hind-cast” to the total time used to measure cure becomes small, due to baseline uncertainty effects that tend to cancel one another at longer relative times
- When uncertainties are properly considered, there is no major discrepancy with observed values, although all large errors were under-predictions



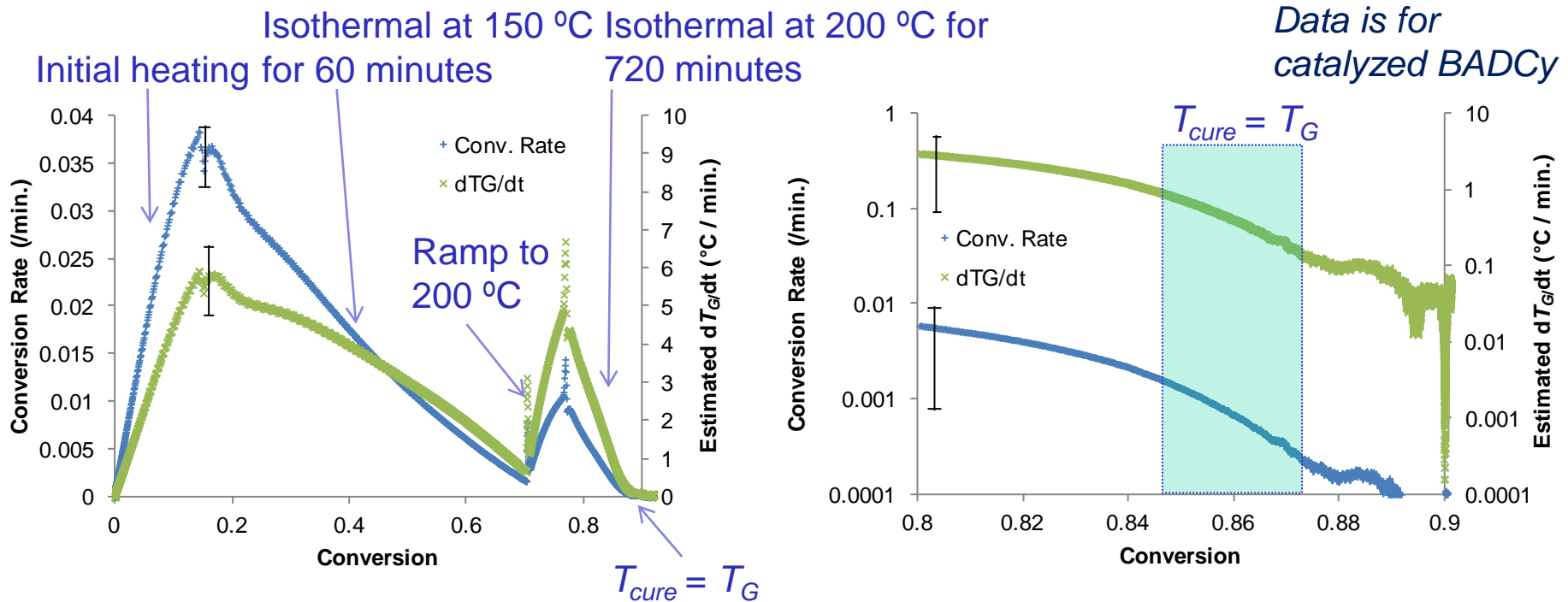
Evolution of T_G During Isothermal Cure of BADCy at 150 °C



- The most common forms of kinetic analysis involve tracking key parameters with respect to conversion (α)
- Reaction rate (most models indicate proportionality to $(\alpha - \alpha_0)^{-2}$, combined with nonlinear increase in T_G with α , results in a nearly linear change in dT_G/dt with α , and an intercept at a conversion of 0.75 ($T_G = 142$ °C)
- At 150 °C, cure rates are so slow that, after vitrification, the cure kinetics cannot be resolved, with uncertainty of around 3-5 x, and even slight baseline shifts overwhelming the signal (Note: error bars generated by sensitivity analysis, and are systematic within series)



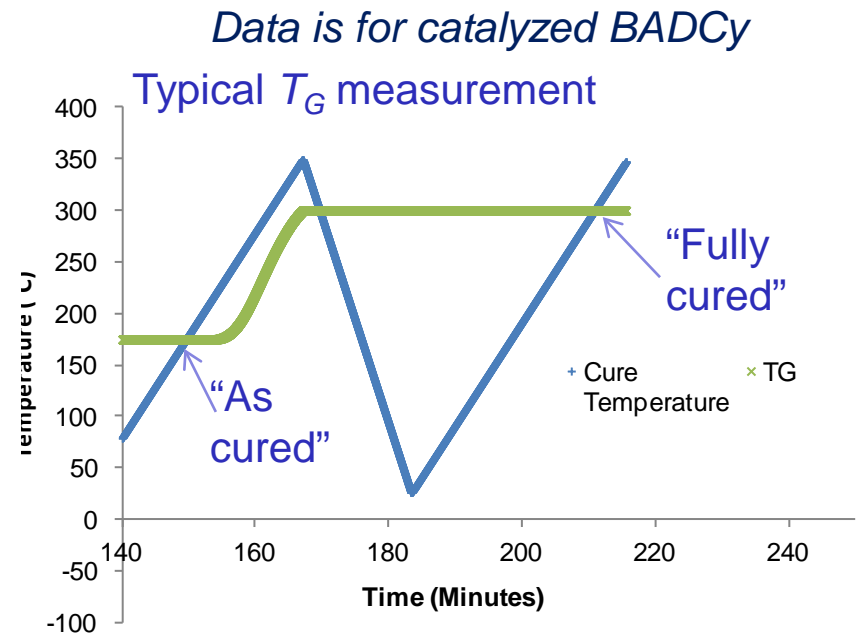
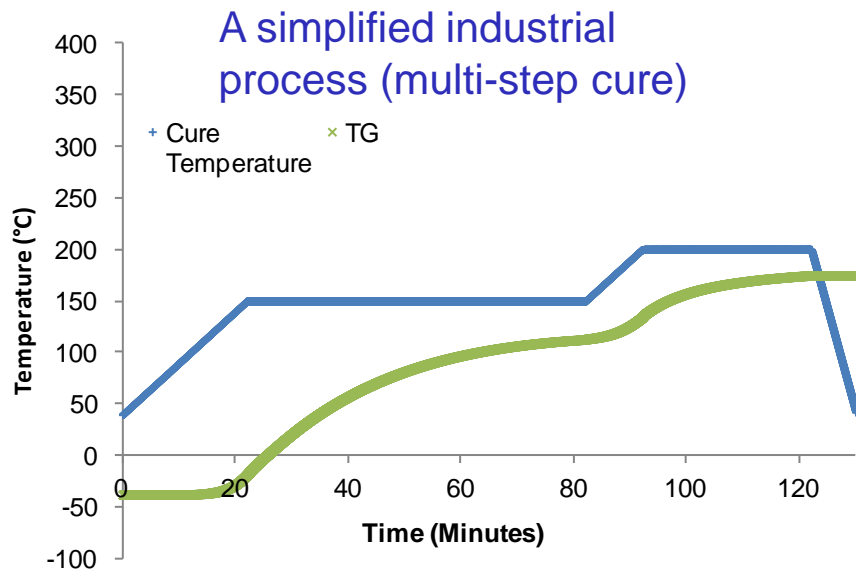
Evolution of T_G During Isothermal Cure of BADCy at 200 °C



- Again, roughly linear change in dT_G/dt with conversion with an intercept at a conversion of 0.87 ($T_G = 203$ °C), but note that the final T_G is in fact much higher, at 246 °C
- At 200 °C, cure rates are high enough that, even with a systematic 5-10 x uncertainty, there appears to be a significant slowing of cure (but not a complete stop) due to vitrification, which can be described by a simple “activated mode” Arrhenius model
- A ~ 0.1 °C / min. increase in T_G after vitrification, with a 10x rate reduction for every ~ 25 °C increase in T_G , is consistent with observed behavior



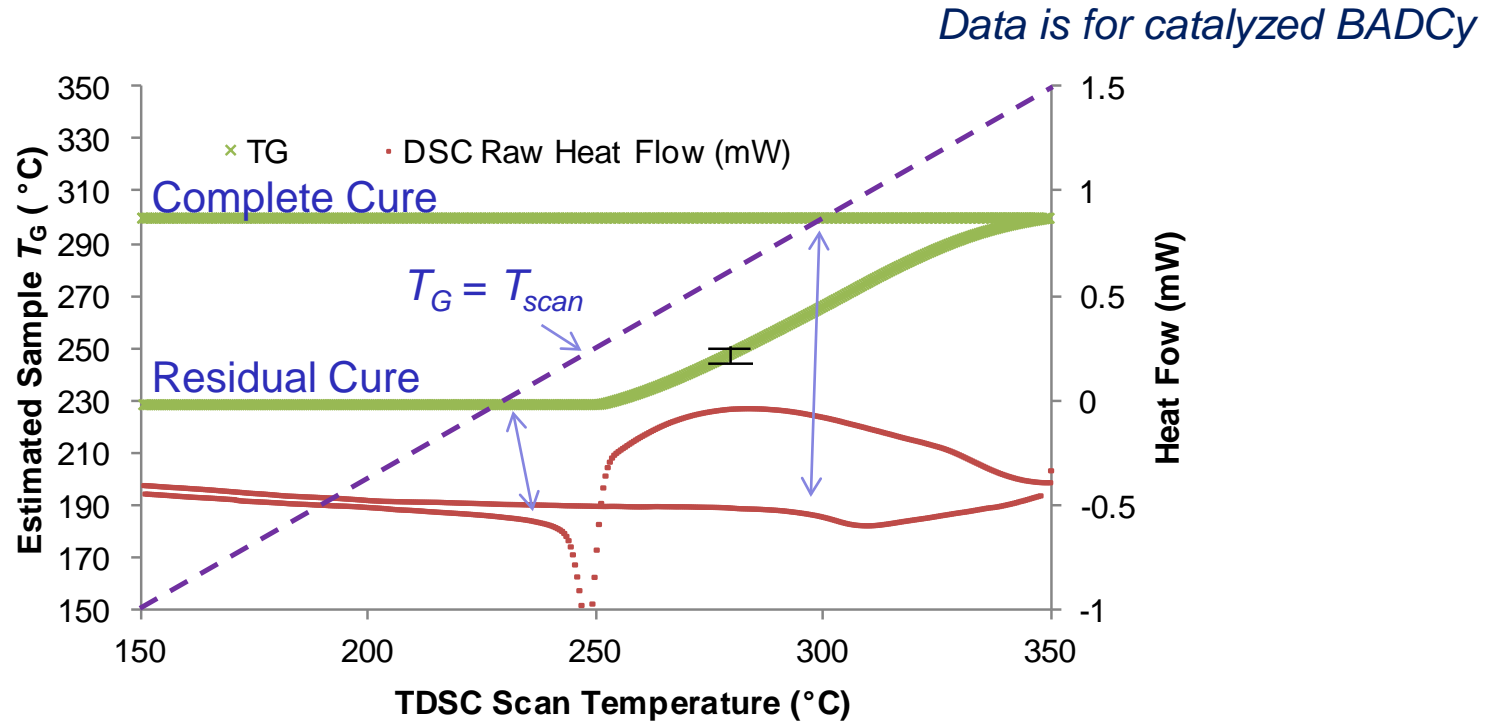
Thermosets Have a T_G Envelope – So T_G Can Change as You Measure It!



- Isothermal steps help to smooth spatial variations and ensure conversion targets are reached
- Complete conversion is desired but often not achieved as $T_G > T_{cure}$
- T_G usually measured after the fact
- Continuous ramp used to complete wide scan of possible temperature values in a short time; heating rate still limited by thermal gradients
- No change in conversion is desired during heating, but *in-situ* cure happens anyway
- Measured T_G may not be accurate



T_G Evolution in BADCy During Residual Cure



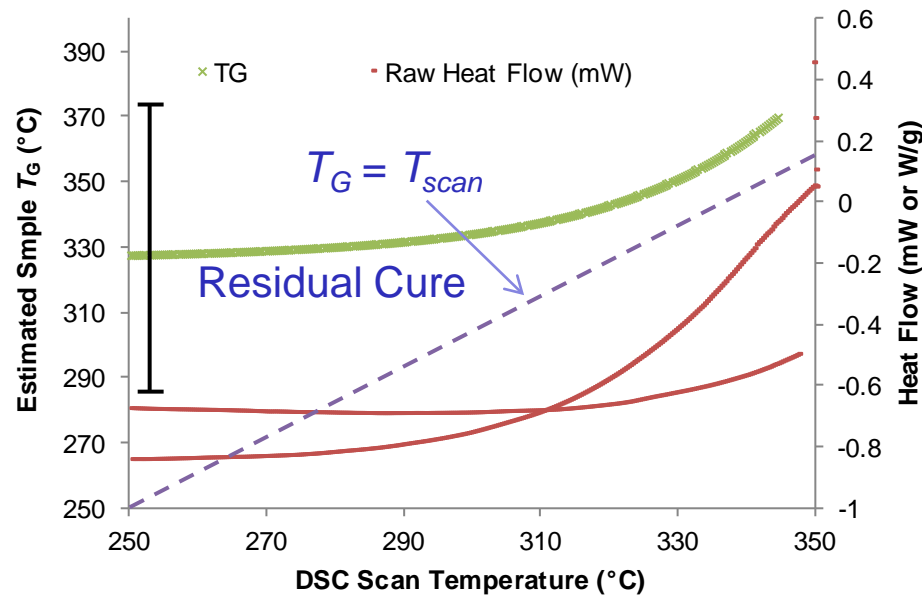
- Only when the scan temperature and T_G coincide is a signal generated. For thermoplastics, with a T_G that does not change, this fact is trivial, but for incompletely cured thermosets, it matters a great deal!
- Note how the T_G increases almost as fast as the scan temperature during residual cure



T_G Evolution in ESR-255 During Residual Cure



*Data is for
uncatalyzed
ESR-255*



- No clear signal corresponding to a T_G is observed in DSC traces, either during, or after, residual cure
- Note how the T_G increases fast enough that it never coincides with the scan temperature over the given range
- The “moving target” nature of the T_G means that the uncertainty in the “as cured” value remains, although the model indicates that the onset of heat flow is a reasonable guess for the “as cured” value



Dimensionless Analysis of T_G Evolution During Residual Cure



$d\alpha/dt$ = reaction rate (variable with conversion, generally ~2% / minute or less after vitrification)

T_{G0} = monomer glass transition temperature (-50 to 0 °C typical for cyanate esters)

$T_{G\infty}$ = glass transition temperature of fully cured network (may not be physically meaningful, typically 250 – 550 °C for cyanate esters)

λ = diBenedetto parameter (typically 0.3 for cyanate esters, dimensionless)

dT/dt = heating rate

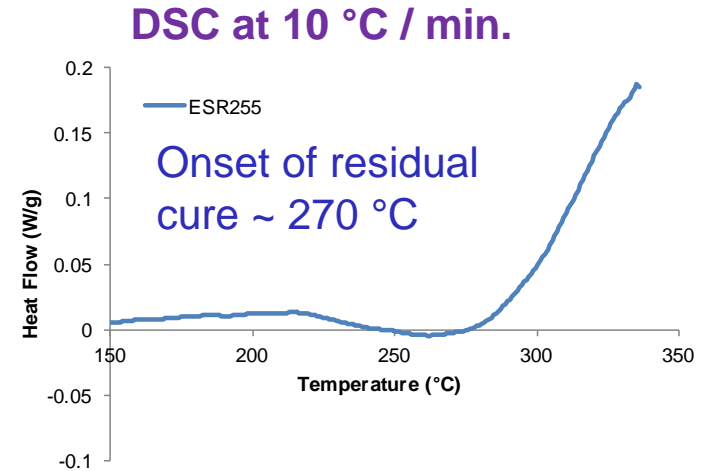
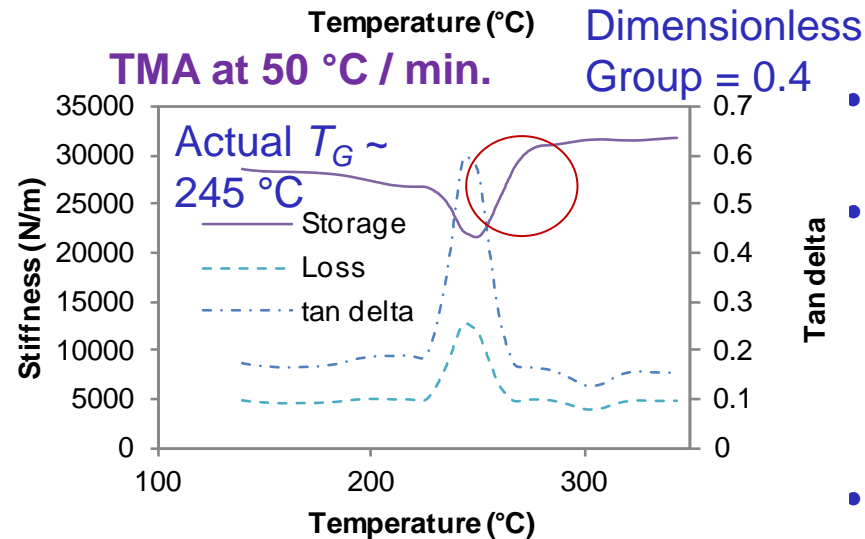
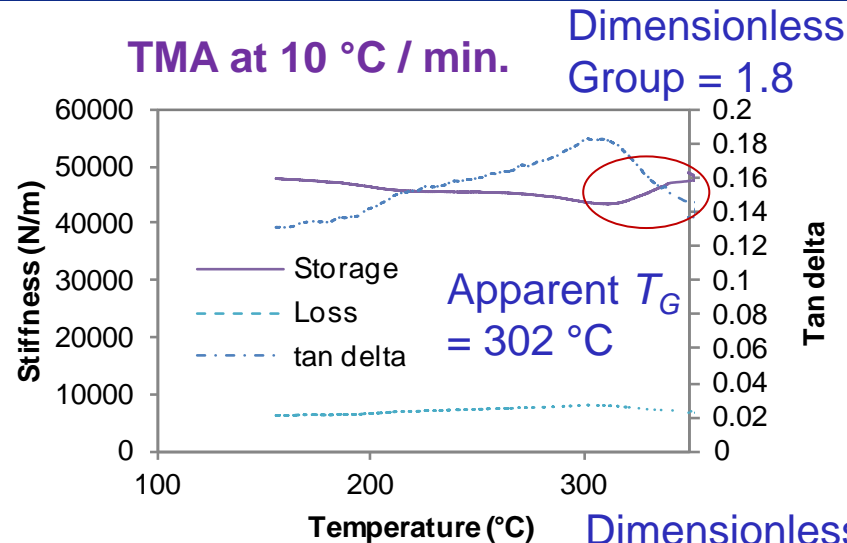
Key dimensionless group:

$$\frac{(d\alpha/dt) (T_{G\infty} - T_{G0})}{\lambda (dT/dt)}$$

- The dimensionless group represents the ratio of the rate at which T_G increases to the rate at which sample temperature increases during residual cure
- When the value of this group is larger than one, the T_G can “outrun” the sample heating, leading to large measurement errors
- As the value of this group approaches zero, the T_G becomes stable over the time scale of the heating experiment and is accurately recorded.
- Using typical values for $d\alpha/dt$ and λ , the heating rate needed to avoid significant risk of *in-situ* cure (in °C / min.) is roughly $0.07 * (T_{G\infty} - T_{G0})$, or roughly 25 °C / min. for BADCy, and roughly 40 °C / min for ESR-255. These are roughly consistent with experience.



Example: T_G Measurements for ESR-255 Cured 24 hrs at 210 °C



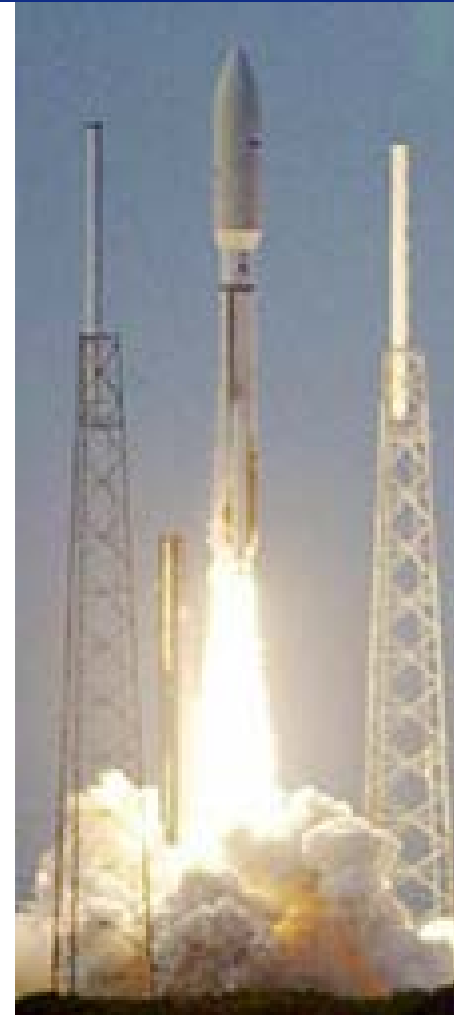
- Using a heating rate that is too slow causes a very significant over-estimate of T_G
- Note that the effects of residual cure are clearly visible in the TMA traces, and include
 - Overly broad tan delta peak with noticeable low-temperature shoulder
 - Increase in storage after T_G (circled)
- Using DSC in combination with TMA, it is clear that the “as cured” T_G cannot be 300 °C



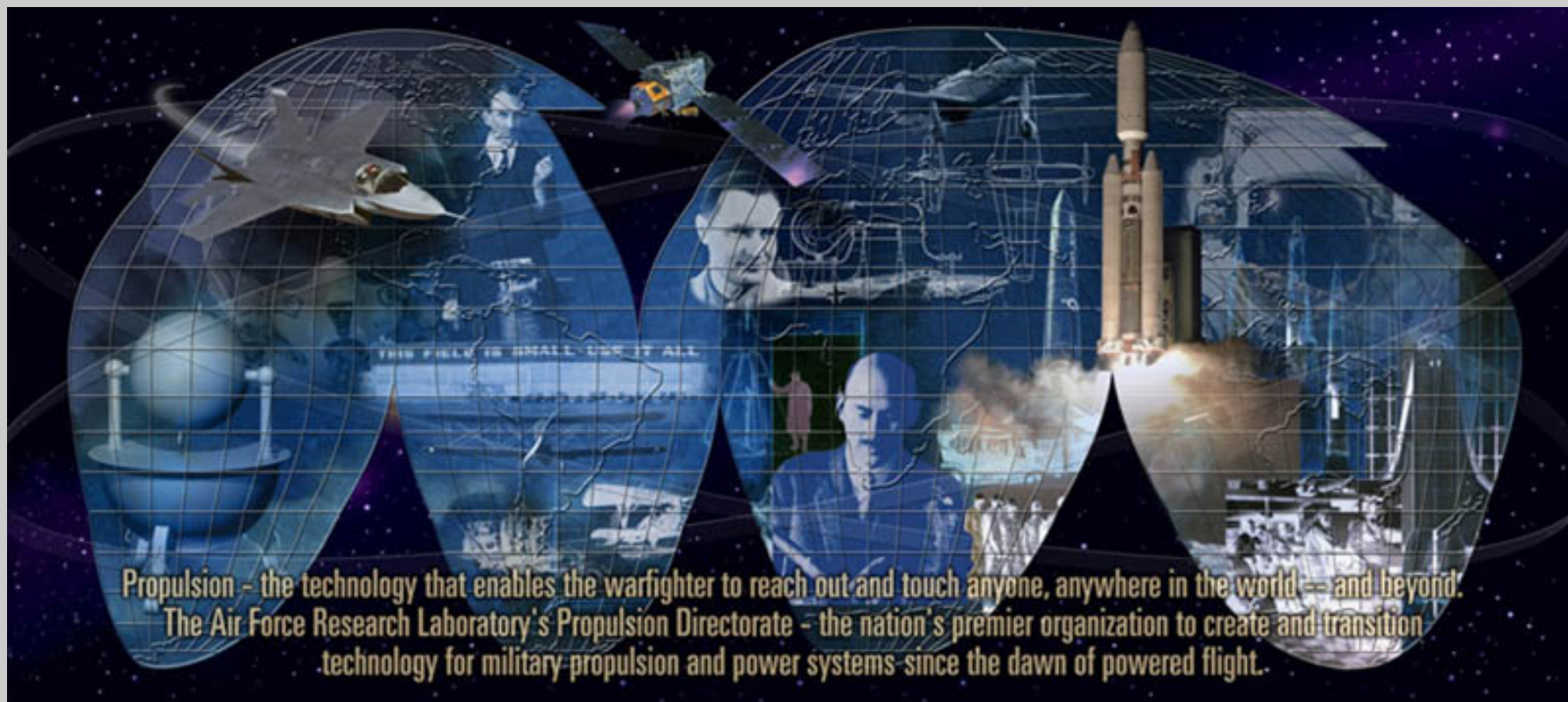
Implications for Composite Resin Development



- A key feature of cure schedules for high-temperature resins such as cyanate esters is passage through the vitrification point
 - Cure of vitrified samples often has the opposite of the intended effect (e.g. water uptake increases with further conversion, rather than decreases)
 - Because many high-temperature resins will cure significantly after vitrification, the assumption that industrial cure schedules always avoid it may need to be checked
 - Cure below the glass transition temperature is a significant issue for characterization of high-temperature composite resins, and can lead to significant over-estimates of thermo-mechanical performance
 - Hot / wet performance is often the limiting factor for many thermosetting resin systems; both “knockdowns” and “wet” property values may be affected by *in situ* cure (this issue needs more attention).



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